SCALE UP STUDY OF SALT ADDED BATCH DISTILLATION OF AZEOTROPIC MIXTURE: ISOPROPANOL/WATER

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LIST OF ABBREVIATIONS

CBD	Conventional Batch Distillation
DI	Deionised
DMSO	Dimethyl Sulfoxide
EMChiE	European Meeting on Chemical Industry and Environment
FKKSA	Faculty of Chemical & Natural Resources Engineering (Fakulti Kejuruteraan Kimia & Sumber Asli)
IL	Ionic Liquid
IPA	Isopropanol
RCM	Residue Curve Map
VLE	Vapour Liquid Equilibrium

LIST OF SYMBOLS

Symbols

n_j	Number of moles of components *j*
v, v_+, v_-	Number of moles of ions, cation and anion
x_j	Mole fraction of component *j* in liquid
y_i	Mole fraction of solvent *i* in vapour
z_i	Mole fraction of solvent *i* in mixed solvent

Subscripts

1	Isopropanol (non-electrolyte)
2	Water
3	Salt
+, -	Cation and anion, respectively

Superscript

'	Vapour phase

KAJIAN PENSKALAAN UNTUK PROSES BATCH PENYULINGAN DENGAN PEENAMBAHAN GARAM BAGI CAMPURAN BERAZEOTROP: ISOPROPANOL / AIR

ABSTRAK

Pemulihan pelarut sering diamalkan dalam industri kimia terutamanya dalam industri pembuatan sarung tangan dan kateter. Walau bagaimanapun, fenomena azeotrop dalam campuran (campuran binari isopropanol-air) merumitkan proses pemisahan. Proses penyulingan secara 'batch' yang konvensional adalah tidak lagi berkesan dalam memulihkan pelarut. Selain itu, pelarut yang tidak dipulihkan akan berakhir sebagai sisa toksik dan pembuangan sisa toksik sebegini membawa impak yang amat bahaya kepada alam sekitar. Kerja eksperimen telah dijalankan dan kajian penskalaan telah dilakukan dalam usaha untuk menyelesaikan masalah ini. Dua objektif dalam kajian ini adalah: (a) menentukan kepekatan garam yang optimum untuk menyuling campuran berazeotrop IPA-air supaya memulihkan ketulenan IPA lebih daripada 90% mol dengan menggunakan penyulingan secara 'batch', dan (b) mengkaji tentang penskalaan unit penyulingan untuk sistem IPA-air dari skala makmal kepada skala loji pandu. Dua peringkat prosedur, iaitu eksperimen berskala makmal dan eksperimen loji pandu, telah dijalankan. Kepekatan garam yang optimum yang diperlukan untuk memecahkan titik azeotrop campuran IPA-air smekain berkurangan selaras dengan peningkatan z_1. Untuk eksperimen berskala makmal, larutan garam dilarutkan dalam campuran IPA-air dan tiada nisbah refluks boleh dikawal kerana radas yang ringkas digunakan. Keputusan menunjukkan bahawa 2.5 mol% dan 1.57 mol% garam kalsium klorida telah berjaya memulihkan 91% mol IPA dari sistem IPA-air yang masing-masing bernilai z_1 = 0.51 dan 0.60. Titik azeotrop campuran binari telah berjaya dipecahkan oleh penambahan larutan garam kalsium klorida. Untuk loji pandu, larutan garam ditambahkan ke bahagian atas turus penyulingan dan nisbah refluks mutlak telah digunakan untuk meningkatkan kecekapan pemindahan haba dan jisim dalam proses penyulingan. Walau bagaimanapun, pendekatan ini tidak berjaya dalam memulihkan ketulenan IPA yang tinggi, di mana fenomena ini boleh dijelaskan oleh ralat dalam data sistem binari kepada sistem multikomponen.

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ABSTRACT

Solvent recovery is often practised in chemical industry especially in glove and catheter manufacturing. However, azeotropic behaviour in mixture (isopropanol-water binary mixture) complicates the separation process. Conventional batch distillation is no longer effective in recovering the solvent. Moreover, the unrecovered solvent will end up as toxic waste and disposal of such toxic waste is jeopardising to the environment. Experimental works were carried out and scaling up study was performed in order to solve these problems. The research objectives are twofold: (a) to determine optimum salt concentration for distilling IPA-water azeotropic mixture by using salt added batch distillation to recover IPA for purity more than 90 mol%, and (b) to study scaling up of salt added batch distillation unit for IPA-water azeotropic mixture from a laboratory scale to pilot plant scale. Two stages of procedures, which are laboratory scale and pilot plant experiments, were carried out. The optimum salt concentration and the scaling up were studied. The optimum salt concentration needed to break the azeotropic point of IPA-water mixture is generally decreasing as z_1 is higher. Salt solution was dissolved to the still before distillation using laboratory scale and no reflux ratio can be controlled due to simpler apparatus. Results showed that 2.5 mol% and 1.57 mol% of calcium chloride salt has successfully recover 91 mol% of IPA from a IPA-water system with z_1 = 0.51 and 0.60, respectively. The binary mixture azeotropic point is successfully broken down by calcium chloride salt addition. In pilot plant, salt solution was added near to the top of column and total reflux ratio was applied to enhance mass and heat transfer in salt effect distillation. However, it did not succeeded in recovering high purity of IPA, probably due to errors in the extension of binary data to multi-component systems.

CHAPTER 1

INTRODUCTION

1.1 Background

Distillation is the most commonly used separation process in the chemical industries. Distillation separates two or more liquid components in a mixture using the principle of relative volatility or boiling points of each component. However, some mixtures exhibit one or more azeotropes, a state at which the coexisting liquid and vapour phases are of equal compositions (Vivek, Madhura, & Lionel, 2009). In the organic chemical industry, separation of azeotropic and close-boiling point mixtures is frequently encountered (Skouras, Kiva & Skogestad, 2005). Therefore, separate homogenous azeotropic mixtures using distillation is viable by adding an extraneous component, referred to as an entrainer or mass separating agent, to facilitate the separation process (Vivek et al, 2009). This is significant because it is a common solvent recovery technology that is typically used in processing industries, such as pharmaceutical, food and specialty chemical industries (Ma ŕa & Tah, 2010).

This research was conducted in Universiti Malaysia Pahang, Gambang campus for the Final Year Project. This research studied on the scaling up of a salt-added batch distillation for azeotropic IPA-water mixtures. Experimental works were carried out in Faculty of Chemical and Natural Resources Engineering (FKKSA) laboratory by distilling an azeotropic IPA-water mixture using a batch distillation unit. The optimum salt concentration needed to give 'salting out' effect to IPA-water mixture for distillation was determined. Scaling up study of such experiments from laboratory scale to pilot plant scale was conducted. This research was completed within two semesters.

1.2 Problem Statements

IPA is widely used in the semi-conductor industry as a cleaning agent. Pure IPA is recovered from the waste IPA-water mixture containing water (Luybern & Chien, 2010). The recovery and reuse of organic solvent is generally practised in processing industries because of the increasing solvent cost and potential solvent shortages. In most industries, however, azeotropy in distillation complicates the recovery of solvents. This in turn results in the unrecovered solvents end up as toxic chemical waste. Disposal of such toxic waste is often results in violation of air-, water-, or land-pollution regulation (Hilmen, 2000).

On the other hand, the scale-up of the distillation process of IPA-water binary system from laboratory scale to pilot plant scale and commercial scale is still an unsolved problem due to the insufficient of scaling up data. One of the most essential

questions is whether the performance of large scale equipment can be predicted with the same approach as applied in the laboratory scale (Sundmacher & Kienle, 2003).

IPA recovery is a real industrial problem in rubber industry, such as glove and catheter manufacturing. However, azeotropy has complicated the solvent recovery. A solution from experiment and pilot plant study is needed.

1.3 Research Objectives

The research objectives were twofold:

i. To determine optimum salt concentration needed for distilling IPA-water azeotropic mixture having an industrial IPA-water composition by using salt added batch distillation to recover IPA for purity more than 90 mol%.

ii. To study scaling up of salt added batch distillation unit for IPA-water azeotropic mixture from a laboratory scale to pilot plant scale.

1.4 Scope of Study

There were three main scopes for this research. There are a few of separation processes that can be used to separate azeotropic mixture, and salt added batch distillation is chosen for this study. Apart from that, calcium chloride ($CaCl_2$), a common type of salt, is chosen as the entrainer because it has a high availability and good separation performance. On the other hand, there are two types of scale up parameters: design and operation. Design parameters such as reflux ratio, number of stages and concentration of $CaCl_2$ salt to be introduced to the distillation column, as well as operation parameters such as salt addition method are also being studied.

1.5 Significance of Study

This study has several significances from the economy, environment and engineering aspects. Firstly, this research can help in saving solvent cost by successfully separating azeotropic IPA-water mixture using salt-added batch distillation to recover IPA more than 90 mol%. Apart from that, this research reduces the unrecovered solvents which are a toxic chemical waste that is harmful to the environment.

1.6 Summary

Optimum salt concentration needed for distilling IPA-water azeotropic mixture has been determined and scaling up study of salt added batch distillation unit from a laboratory scale to pilot plant scale has been performed. Optimum salt concentration was determined through experimental works, data collection and analysis. Salt-added batch distillation, IPA-water azeotropic mixture, and calcium chloride$_2$ salt are the scopes for this research. This research has successfully recovers the IPA for a purity more than 90 mol%. It helps in saving a significant solvent cost and reduces the disposal of toxic waste.

CHAPTER 2

LITERATURE REVIEW

2.1 Introduction

Industrial production of chemicals involves purification and recovery of the products, by-products and unreacted raw materials. Therefore, solvent recovery is becoming a major issue in the pharmaceutical and specialty chemical industries. However, solvent recovery by conventional batch distillation (CBD) is limited by the frequent presence of azeotropes in the used solvent mixtures. As a result, most distillation processes for the separation of azeotropic or difficult zeotropic mixtures involve the addition of an entrainer (homogeneous and heterogeneous azeotropic distillation or extractive distillation).

In a European meeting on Chemical Industry and Environment (EMChiE), Van Baelen et al. (2010) pinpointed that the strongest commercial argument for recovering solvents is the direct cost savings. In some processes with intensive solvent use, the cost of the solvent can be a significant proportion of the overall

product cost. They further explained that another compelling reason for recovering solvents is the increasing environmental legislation against emissions.

2.2 Batch Distillation

Mujtaba (2004) stated that batch distillation is possibly the most widely used operation for liquid mixtures separation. Batch distillation is commonly utilized for the production of fine chemicals and specialized products such as essential oils, alcoholic beverages, perfume, pharmaceutical and petroleum products. Mujtaba's study (as cited in Lucet, Charamel, Champuis, Guido & Loreau, 1992) found that batch distillation is the most frequent separation method in batch process.

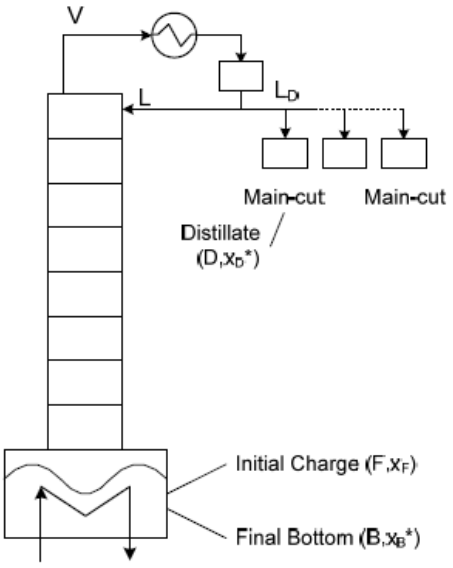

Figure 2.1 A conventional batch distillation (CBD) unit

(Source: Mujtaba, 2004)

Figure 2.1 shows a conventional batch distillation (CBD) unit. The essential parts of a CBD column are as followed:

i. A bottom receiver/reboiler which is charged with the feed to be processed and which provides the heat transfer surface.

ii. A rectifying column (either a tray or packed column) superimposed on the reboiler, coupled with either a total condenser or a partial condenser system.

iii. A series of product accumulator tanks connected to the product streams to collect the main and/or the intermediate distillate fractions.

Batch distillation is usually started by charging a batch of liquid feed into the tank. The more volatile component in the mixture will be vapourised and rising through a column above the tank combines with reflux coming down the column to effect concentration. Operation of such a column involves running the fractionation until a required amount has been distilled off. During the operation, the overhead composition varies and generally a number of cuts are made. Some of the cuts are desired products (main-cuts) while others are intermediate fractions (off-cuts) that can be recycled to subsequent batches to obtain further separation. A residual bottom fraction may or may not be recovered as product (Mujtaba, 1989; 2004).

2.2.1 Advantages of Batch Distillation

Although in the process industries, most distillation systems are continuous, batch systems are preferred for the distillation of relatively small quantities of solvents. Ma ŕa and Tah's journal (as cited in Kim & Diwekar, 2000) stated that the most outstanding feature of batch distillation is its flexibility in design and operation. Its high flexibility enables it can be used to recover plenty of different solvents. It is also very practical in pilot-plant operations and in processes where the compositions of the materials to be separated vary widely or the main product contains only small amounts of impurities (as cited in Kister, 1992). Apart from that, multi-component mixtures can be separated using one single batch column (as cited in Stichlmair & Fair, 1998). A batch system can often separate many components in one column, albeit with a premium on utilities. Nevertheless, in order to separate a multi-component mixture of *n* components by continuous distillation, a minimum of *n*-1 separate columns are required, which involves a significantly higher capital cost. While a batch system is more energy intensive than a continuous system, steam costs generally are less significant on a small operation.

2.3 Azeotropy

All liquid mixtures have intermolecular forces of attraction. When two or more liquid components are mixed, the intermolecular interactions may cause the mixture to form certain "inseparable" compositions where the vapour and liquid compositions at equilibrium are equal within a given pressure and temperature range.

These specific mixture compositions are termed azeotropes, and the phenomena is called azeotropy.

2.3.1 IPA-Water Binary System

At atmospheric condition, a binary mixture of IPA–water forms a homogeneous minimum-boiling azeotrope at 87.4–87.7 mass% and 80.3–80.4 ℃. Some investigations have reported that IPA–water azeotrope can also be broken with other azeotropic distillations to form heterogeneous azeotropic systems by adding one of the following entrainers: isopropyl ether, benzene, methyl ethyl ketone, and isopropyl acetate.

2.4 Vapour Liquid Equilibrium (VLE) Diagram

To understand the nature of simple distillation, fractional distillation and azeotropes, a vapour/liquid diagram for pairs of solvents is studied. Figure 2.2 shows a typical VLE diagram for 2 solvents, A and B where A is the lower boiling material. The bottom of the graph shows the liquid state and the top of the graph shows the vapour state. The area in between the two curves shows what is happening in the distillation column. The x-axes at the top and bottom represent the composition of component A and B in the mixture, respectively. The y-axis is the temperature of the mixture.

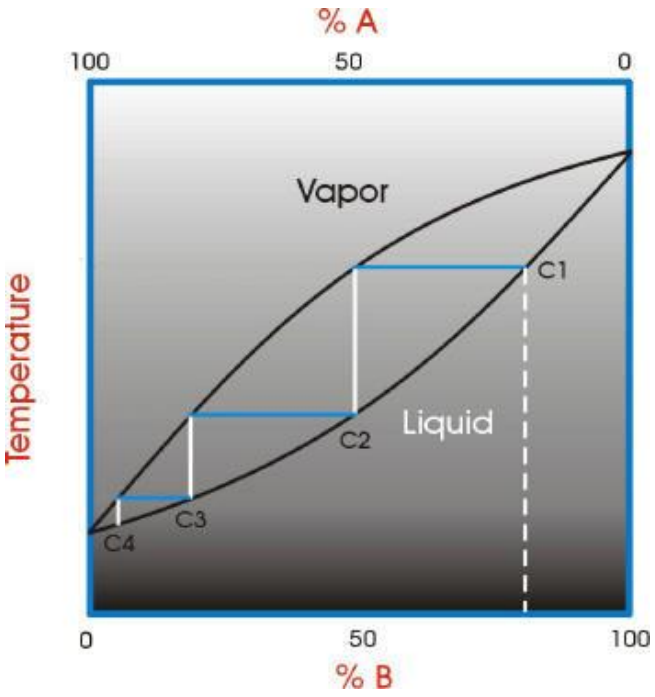

Figure 2.2 A typical VLE diagram

(Source: Smallwood, 2002)

A liquid mixture of A and B with certain temperature and a composition corresponds to the point C1, where its temperature can be read off horizontally to the y-axis, while its component composition can be read off by following the dashed line down to the x-axis at the top and bottom for composition of A and B, respectively. From the point C1, the distillation is happened by tracing the horizontal line to the left until it reaches the vapour curve. This process has improved the concentration of A, the lower boiling component. The material is then condensed by following the solid vertical line down to the liquid curve. If this was simple distillation, distillation could stop now. It can be seen that the purification effected by the simple distillation of such a mixture of volatile liquids is very imperfect.

In a fractional distillation, however, the distillation process continues. The condensed material is vapourised again by following the horizontal line across from the liquid curve at C2 to the vapour curve. There is another improvement in the concentration of the lower boiling component A. The vapour is condensed again by following the vertical line down to the liquid curve at point C3. These repeating vapourisation-condensation steps continue. The number of times that the process of vaporisation and condensation occurs depends on the efficiency of the distillation column. The more efficient the distillation column, the more times this happens and the purer the final product will be.

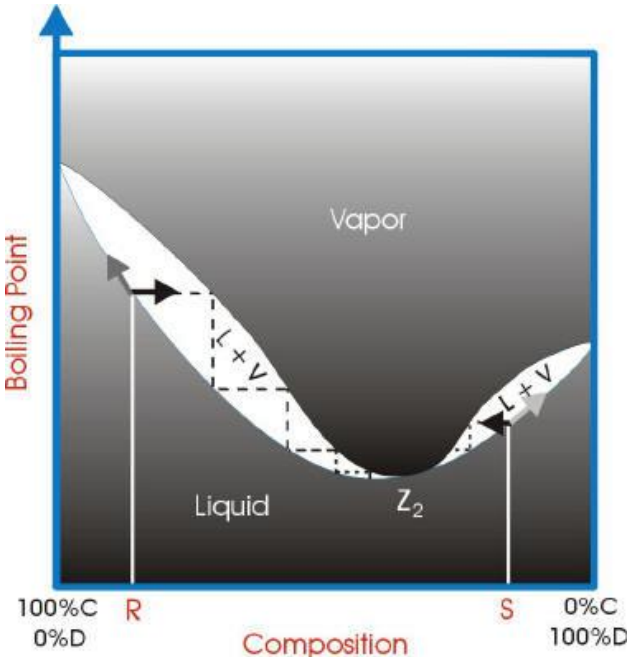

Figure 2.3 A VLE diagram showing azeotrope point, Z_2

(Source: Smallwood, 2002)

Figure 2.3 depicts a VLE diagram showing azeotropic point. For an azeotropic mixture, the vapour liquid curves are not ideal and have a point where the vapour curve meets the liquid curve. The component compositions, temperature and

pressure of liquid phase are equal to those of vapour phase. This point is called the azeotrope point, as shown as point Z_2.

2.5 Azeotropic Distillation

In the thesis written by Hilmen (2000), he stated that further separation of azeotropic mixture by ordinary distillation is no longer possible since no enrichment of the vapour phase occurs at this point. Therefore, in most cases, azeotropic mixtures require special methods to facilitate their separation. Such methods utilize a mass separating agent other than energy that causes or enhances a selective mass transfer of the azeotrope-forming components.

In the definition of McGraw-Hill Concise Encyclopedia of Science and Technology (2005), azeotropic distillation is any of several processes by which liquid mixtures containing azeotropes may be separated into their pure components with the aid of an additional substance (called the entrainer, the solvent, or the mass separating agent) to facilitate the distillation. Therefore, it is often possible to 'break' the azeotrope by adding a carefully selected entrainer to the mixture, thereby achieve the desired separation.

Entrainers fall into at least four distinct categories that may be identified by the way in which they make the separation. These categories are: (1) liquid entrainers that do not induce liquid-phase separation, used in homogeneous azeotropic distillations, of which classical extractive distillation is a special case; (2) liquid

entrainers that do induce a liquid-phase separation, used in heterogeneous azeotropic distillations; (3) entrainers that react with one of the components; and (4) entrainers that dissociate ionically, that is, salts. Within each of these categories, not all entrainers will make the separation possible, that is, not all entrainers will break the azeotrope possible (McGraw-Hill Concise Encyclopedia of Science and Technology, 2005, pp 236-237).

In a journal reviewing about batch distillation written by Skouras et al. (2005), they stated that a process is termed extractive batch distillation when a heavy entrainer is added continuously in the top section of the batch column,. When the entrainer forms a homoazeotrope with at least one of the original components and is added batch-wise to the original mixture, the process is called homogeneous azeotropic or homoazeotropic batch distillation. When the entrainer forms a binary heteroazeotrope with at least one (and preferably with only one) of the original components or a ternary heteroazeotrope and is added batch-wise to the original mixture, the process is called heterogeneous azeotropic or heteroazeotropic batch distillation.

In order to determine whether a given entrainer is practicable, a schematic representation known as a residue curve map (RCM) for a mixture undergoing simple distillation is created. The path of liquid compositions starting from some initial point is the residue curve. The collection of all such curves for a given mixture is known as a residue curve map. These maps contain exactly the same information as the corresponding phase diagram for the mixture, but they represent it in such a way that it is more useful for understanding and designing distillation systems